Inside look

Chemistry and Biochemistry of Vanilla Flavor

A survey of the latest research

Arvind Ranadive, Premier Vanilla Inc.

The characteristic aroma and flavor of vanilla is the result of various chemical and biochemical processes that take place during the curing and conditioning of vanilla beans. Vanillin is an important constituent of the cured vanilla bean, contributing greatly to its characteristic aroma and taste. Although the presence of vanillin in the vanilla bean greatly enhances the quality of vanilla, its absence does not change the basic vanilla character or render the beans worthless. A number of other major, minor and trace constituents play very significant roles in imparting vanilla with its characteristic aroma and flavor.

Vanilla species, growing conditions, soil nutrition, harvest maturity of the beans and the curing method used determine the relative concentrations of various flavor constituents of cured vanilla. The cured beans contain protein, sugars, lignocellulosic fibers, cellulose, organic acids, vanillin and other monohydroxyphenols, fixed oil, wax, resin, gum, pigments, tannins, minerals, volatile aromatics and essential oil. The general composition of whole vanilla beans from different regions has been reported in the literature.[1,2]

The vanilla constituents responsible for aroma and flavor include volatiles such as aromatic carbonyls, aromatic alcohols, aromatic acids, aromatic esters, phenols and phenol ethers, aliphatic alcohols, carbonyls, acids, esters and lactones, aromatic hydrocarbons, terpenoids, aliphatic hydrocarbons and heterocyclics. The nonvolatile constituents important in vanilla flavor are tannins, polyphenols, resins and free amino acids. All of these constituents together produce the delicate, rich and mellow aroma with sweet spicy, woody and balsamic notes. A listing of vanilla flavor terminology is presented in T-1.

Vanilla flavor terminology **T-1**

anisic
balsamic
caramelized
chocolate
creamy
floral
haylike
prune/raisin
resinous
smoky
sweet
tealike
vanillin
woody

Chemical Constituents of Vanilla Flavor

The most abundant flavor and aroma chemical present in cured vanilla beans is vanillin, which imparts a very sweet, creamy character and enhances the flavor strength of vanilla. The vanillin content of cured beans of different origins varies from 0.3 percent to 3 percent.[1-5] The vanillin content of beans depends upon a number of variables, such as species, bean maturity at the time of harvest and curing process. For example, *Vanilla planifolia* Andrews produces beans with the highest vanillin content, while *V. tahitensis* and *V. pompona* produce moderate and low levels of vanillin, respectively. Large variation in vanillin content observed within a species depends mostly on the bean maturity at the harvest time and the sophistication of curing techniques used. Fully mature beans with yellow blossom ends produce the highest amount of vanillin, whereas beans harvested before maturity produce lower amounts of vanillin. Beans harvested only four to five months after pollination contain trace amounts of vanillin or its precursor, glucovanillin.

Other major aromatic constituents of vanilla beans are p-hydroxybenzaldehyde (0.12-0.15 percent), vanillic acid (0.1 percent), p-hydroxybenzoic acid, p-hydroxy benzyl methyl ether and acetic acid (the latter three each 0.02 percent). Klimes and Lamparsky have identified about 170 volatile chemicals in Madagascar beans.[6] Aside from the previously mentioned major constituents, approximately 20 more are present in quantities ranging from 1 ppm to 10 ppm; the rest are present in trace quantities. Several investigators have identified various volatile chemicals present in three commercially important species, which are presented in comprehensive form in T-2.

Schulte-Elte et al. found two diastereoisomeric vitispiranes (2,10,10-trimethyl-6methylidene-1-oxaspiro [4.5]dec-7-enes) in vanilla volatiles isolated from Bourbon vanilla oleoresin at a level of approximately 1 ppm.[7] The authors found these ionone-like spiro-ethers to be important constituents of vanilla aroma. The *cis* and *trans* isomers were found to have different aromatic characters. Sculte-Elte et al. described the *cis* compound as having a green odor of chrysanthemum with a flowery-fruity wine note, while the *trans* compound was found to have a heavy scent of exotic flowers with an earthy-woody undertone and a note of dry wines. It would be interesting to see whether vitispiranes are present in cured beans of other vanilla species and other geographic areas.

Galetto and Hoffman identified four benzyl ethers identified as vanillyl ethyl ether (3 ppm), vanillyl methyl ether (13 ppm), p-hydroxybenzyl ethyl ether and p-hydroxybenzyl methyl ether (143 ppm) isolated from commercial Bourbon extract.[8] Klimes and Lamparsky also detected these four benzyl ethers in vanilla extract.[6] These ethers are described as having "sweet, vanillalike flavor notes with creamy, coconut secondary flavor characteristics." Their overall impact on vanilla flavor was found to be less dramatic than vanillin.

It appears from various studies on the chemical constituents that, within a species, the characteristic aroma and flavor profiles are more a function of quantitative, rather than qualitative, chemical composition. Adedeji et al. have identified anywhere from three to 18 organic compounds unique to various growing regions such as Java, Madagascar, Bali, Mexico, Costa Rica and Tonga, but the flavor impact of these unique compounds on each type of vanilla is not clear.[9] Indian vanilla beans (*V. planifolia* Andrews), despite their high vanillin content, are less sweet than other varieties and lack balsamic notes. There is the possibility that nonvolatile components, such as polyphenols, quinones, free amino acids and free sugars, may show important qualitative and quantitative differences in different species or geographic origins, and thus significantly affect the flavor and aroma character. Balls and Arana found a correlation between the superior

Volatiles identified in the cured beans of genus *Vanilla* [6-8,11-15]

T-2

Aromatic constituents

benzaldehyde
trans-cinnamaldehyde
salicylic aldehyde
anisaldehyde
p-hydroxybenzaldehyde
methyl benzoate
ethyl benzoate
benzyl formate
benzyl cinnamate
cinnamyl cinnamate
phenethyl acetate
methyl *cis*-cinnamate
monoethyl phthalate
di-n-propyl phthalate
methyl vanillate
anisic acid
p-hydroxy benzoic acid
benzoic acid
benzyl alcohol
p-hydroxybenzyl alcohol
phenylethyl alcohol
ethylbenzene
dimethyl benzene
toluene
styrene

vanillin
p-methoxybenzalde
acetophenone

methyl salicylate
benzyl acetate
cinnamyl benzoate
p-hydroxybenzyl acetate
methyl phenylacetate
methyl *trans*-cinnamate
diethyl phthalate
di-n-butyl phthalate
salicylic acid
vanillic acid
cinnamic acid
anisic alcohol
p-methoxybenzyl alcohol
vanillyl alcohol
benzene
propylbenzene
trimethyl benzene
p-ethyltoluene
naphthalene

Heterocyclics

furfural
5-hydroxymethyl
2-acetylfuran
furfuryl hydroxymethyl ketone

thiophene
cis-vitispirane
methyl nicotinate

5-methyl furfural
furfural furfuryl alcohol
2-pentylfuran
2-hydroxymethyl-5-methylfuran
2-acetylpyrrole
trans-vitispirane

Phenolics

phenol
guaiacol
p-ethylguaiacol
p-vinylguaiacol

anisole
diphenyl ether
p-cresyl isopropyl ether
vanillyl ethyl ether

p-hydroxy benzyl ethyl ether

p-cresol
cresol
p-vinylphenol
vanillin 2,3-butyleneglycol acetal
1,2-dimethoxybenzene

vanillyl methyl ether
p-hydroxybenzyl methyl ether

Lactones

butyralactone

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T-2

Aliphatic constituents

pentan-1-al
heptan-2-one
nonan-2-one
3-penten-2-one
octa-4,6-diene-3-one
1-hydroxypentan-2-one
5-hydroxyheptan-2-one
pentan-1-ol
hexan-1-ol
heptan-1-ol
octan-1-ol
1-octene-3-ol
3-methylbutan-1-ol
formic acid
propionic acid
valeric acid
caproic acid
decanoic acid
myristic acid
methoxyacetic acid
n-amyl acetate
methyl valerate
isopropyl valarate
isobutyl valarate
methyl caproate
methyl heptanoate
methyl laurate
methyl pentadecanoate
methyl heptadecanoate
ethyl methoxyacetate
ethyl lactate
nonane
undecane
tetradecane (two isomers)
hexadecane (two isomers)
octadecane (branched)
docosane (branched)
x-dodecene
x-eicosene

hexan-2-one
octan-2-one
decan-2-one
3-octene-2-one
3-hydroxybutan-2-one
1-hydroxyhexan-2-one
butane-2,3-diol
dodecan-1-ol
pentan-2-ol
nonan-2-ol
prenol
2-methylbutan-1-ol
3-methylpentan-1-ol
acetic acid
butyric acid
isovaleric acid
octanoic acid
lauric acid
glycolic acid
lactic acid
n-hexyl acetate
propyl valerate
butyl valarate
ethyl-2-methyl butyrate
ethyl caproate
methyl nonanoate
methyl myristate
methyl palmitate
methyl glycolate
methyl lactate
ethyl levulinate
decane
dodecane (two isomers)
pentadecane
heptadecane (branched)
eicosane (branched)
x-decene (branched)
x-tetradecene

Terpenoids

α-pinene
limonene
β-phellandrene
p-cymene
citronellol
geraniol
β-cyclocitral
δ-cadinene
myrtenol
terpinen-4-ol

β-pinene
myrcene
α-terpinene
α-curcumene
nerol
β-bisabolol
6,10,14-trimethyl-
pentadecan-2-on
α-muurolene
α-terpineol
linalool

quality of vanilla extract and their higher nonvanillin phenol content.[10] The authors concluded that phenols other than vanillin contribute significantly to the flavor and aroma and are responsible for much of the flavoring value of the extract.

Vanilla resins have a pleasant taste and act as a fixative for vanilla volatiles. Resins are believed to be polymerized polysubstituted phenols present in cured beans. Typically, they are insoluble in water, but are soluble in alcohol and alkalis. The resin content of Bourbon beans is around 1 percent; Java beans contain less than half as much resin. Researchers currently are studying the possibility that higher molecular weight diketones are responsible for balsamic and resinous characters in high-quality vanilla beans and extracts.

The Aroma and Flavor of Vanilla

A number of published reports compare the aroma chemicals of the three vanilla species.[3,12,16] Although all chemicals that might be responsible for characterizing different species are not identified, anisic alcohol, anisic aldehyde, anisic ethers, anisic acid esters and p-hydroxybenzoic acid have been found to be significant in that respect. For example, all of these chemicals are found in trace quantities in *V. planifolia* Andrews species of any geographic origin, while they are present in relative abundance in *V. tahitensis*. As a consequence, Tahitian vanilla has a flowery, perfumey, fragrant heliotropinelike aroma, yet Bourbon vanilla lacks these notes. Heliotropine, however, is not a chemical constituent of vanilla. Adedeji et al. and Tabacchi et al. have confirmed the presence of p-anisyl alcohol, m-anisaldehyde, m-anisate and anisic acid in vanilla.[9,13] Adedeji et al. identified acetic acid, 3-methyl-2-pentanone, methyl pyruvate, anisyl acetate, acetylfuran, methyl furoate, 5-methyl-2(3H)-furanone and six other minor components for the first time as Tahitian vanilla volatiles. Relative abundance of volatiles distinguishing three species is indicated in T-3.

Although one can associate floral notes with anisyl compounds, smoky and phenolic notes to guaiacol and p-cresol, tobaccolike character to nicotine derivatives, sweet notes to vanillin and its derivatives, and balsamic notes and resinous character to higher-molecular-weight diketones, far more work needs to be done to correlate aroma chemicals identified in a particular vanilla bean type to its peculiar aroma and taste. At the Vanilla 2005 conference held in Veracruz, Mexico, in November 2005, Mark Black presented his latest work on this subject.[17] Many known aroma chemicals were identified in cured vanilla beans of different geographic origins and species. Black's work seems to indicate that the preponderance of certain chemicals in each case determines the overall flavor character of those beans. Using gas chromatography/olfactometry, a general relationship was noted between the presence of diacetyl and acetoin and butter notes;

Relative abundance of characterizing volatiles in three vanilla species[13,14,16] **T-3**

	V. planifolia	*V. tahitensis*	*V. pompona*
vanillin	++++	+++	++
anisyl alcohol	-	+++	+
anisic acid	+/-	+++	+
anisic aldehyde	+/-	++	+
p-hydroxy benzoic acid	+	+++	++
p-hydroxy benzaldehyde	++	++	+
protocatechaldehyde	+	++	+
vanilic acid	++	++	+
protochatechuic acid	+/-	+/-	+

Note: number of + signs indicates relative abundance; - sign indicates absence; +/- sign indicates trace

between guaiacol and p-cresol and strong phenolic notes; between pentanal and hexanal and green notes; among limonene, nonanal, decanal and citrus notes; and among vanillin, methyl cinnamate, T-caryophyllene and typical vanilla, balsamic, woody notes.

The characteristic aroma and flavor of vanilla is developed during curing and the extended conditioning period. Hydrolysis during curing of various glucosides gives rise to many aromatic monohydroxyphenols, including vanillin. About 18 aromatic phenolic compounds have been identified in cured vanilla beans.[18] These free phenols are oxidized further by oxidases during curing and conditioning to form various aromatic quinones. Polymerization of some of the oxidized and nonoxidized phenols leads to the formation of resinous compounds with distinct taste attributes. Oxidation and polymerization also lead to the formation of stable pigments.

The accumulation of various aromatic and nonaromatic compounds, organic acids, alcohols, amino compounds, free sugars, etc., provides precursor compounds for etherification, esterification, acidolysis, oxidations, formation of Schiff bases and Strecker degradation reactions during curing and especially during a prolonged conditioning period. Some of the reactions continue in the aqueous-ethanolic extracts produced from the cured beans, as is noticed in the aged extracts, which have a much finer and mellower aroma than the fresh extracts. During aging, esters of higher alcohols are hydrolyzed, and the free acids then combine with lower alcohols, forming new esters; at the same time, the free higher alcohols are oxidized to aldehydes.

Qualitative Variations Among Species

The qualitative differences in the aroma and flavor of vanilla of different species and geographic origins are quite discrete. Various types of beans have been described as follows:

- ***Bourbon vanilla*** (**V. planifolia** ***Andrews***)***:*** This is the terminology used collectively for beans from Madagascar, Réunion, the Comoro Islands and the Seychelles. Bourbon vanilla is sweet, creamy, rich, full-bodied, tobaccolike, somewhat woody and animal, and deep balsamic, and has sweet spicy back notes.

- ***Mexican vanilla*** (**V. planifolia** ***Andrews***)***:*** This type of vanilla is sharp, slightly pungent and sweet spicy, but lacks body compared to Bourbon vanilla.

- ***Java vanilla*** (**V. planifolia** ***Andrews***)***:*** Hailing from the Indonesian islands, this vanilla type is less sweet and creamy than Bourbon vanilla. Java vanilla lacks bouquet, but has a strong woody and slightly smoky character—*and* a freshly sharpened pencil note.

- ***Indian vanilla*** (**V. planifolia** ***Andrews***)***:*** This variety is full-bodied but less sweet and creamy than Bourbon vanilla. Indian vanilla lacks balsamic notes, but has slightly spicy and pungent sour notes.

- ***Uganda vanilla*** (**V. planifolia** ***Andrews***)***:*** Properly cured Uganda beans have aroma and flavor similar to Bourbon vanilla, although less creamy and sweet.

- ***Tahitian vanilla*** (**V. tahitensis**)***:*** This vanilla type is distinctly perfumey and flowery, fragrant, heliotropinelike, with a rather shallow vanilla character.

- ***Papua New Guinea (PNG) vanilla*** (**V. tahitensis, V. hapape** ***or possibly*** **V. politi**)***:*** PNG vanilla is weakly flowery and perfumey, and possesses anisic

notes. It is generally weak in flavor and aroma character.

- **_Guadeloupe vanilla_ (V. pompona):** Produced in Central America, this variety is perfumey and floral, possessing a sweet anisic heliotropinelike fragrance. It lacks body.

A complete listing of vanilla bean aroma terminology is provided in T-4. Characterizing volatile abundance is listed in T-3 (on page 41).

Enzymic Processes Important to the Development of Vanilla Flavor

Several enzymes are involved in the biogenesis of flavor, including glucosidases, oxidases, synthases, methyl transferases, proteases and phenylalanine ammonia lyase. The role of the enzyme β-glucosidase in the development of vanilla aroma and flavor has been studied extensively. The activities of the oxidative enzymes, especially peroxidases and polyphenol oxidase, are monitored during growth and maturation of vanilla beans, but it is not known exactly what flavor development reactions they catalyze.

Besides vanillin, other major volatile constituents of vanilla aroma identified in *V. planifolia* Andrews are p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillic acid (4-hydroxy,3-methoxy benzoic acid), vanillyl alcohol (4-hydroxy,3-methoxy benzyl alcohol) and p-hydroxybenzyl alcohol. All of these are present mostly in their glucosidic form in green vanilla beans. Small amounts are also present in their free form, probably due to some enzymic activity present in green beans. Like vanillin, these other components are freed, almost completely, from their glycosidic form through enzymic catalysis during curing of vanilla beans. In addition, many other chemicals present contribute to overall vanilla aroma.

The important role of β-glucosidase in curing has been studied by Arana, Balls and Arana, Goris, Ranadive et al., and Dignum.[19-22] Arana reported negligible amounts of active β-glucosidase present in the green beans (stage of growth from pollination is not mentioned), but more was present in blossom-end-yellow beans; the greatest amount was present in split blossom-end-yellow beans. Arana also found that there was no active β-glucosidase in the central seed portion and placental tissue of the beans, but was present entirely in the fleshy part of the pods. In addition to hydrolysis of glucovanillin, β-glucosidase also frees many other aglycons from their glucosidic forms during vanilla curing. Arana and Balls also implied that the basis of vanilla curing might be an accelerated rate of overall enzymic oxidation. These important oxidative transformations are attributed to two oxidative enzymes: a peroxidase that uses hydrogen peroxide, and an oxidase that uses atmospheric oxygen.[20,23-25]

For a period of five months, Wild-Altamirano monitored proteinase, glucosidase, peroxidase and polyphenoloxidase activities during the growth of Mexican vanilla pods.[26] He found that proteolytic activity decreased with pod age, and peroxidase activity increased markedly from the third month onward, while both polyphenoloxidase and glucosidase activities increased less notably. On the basis of his data, Wild-Altamirano concluded that proteolysis apparently becomes less important as beans reach maturity, while carbohydrate degradative reactions and oxidative activities become more significant.

Vanilla Bean Aroma Terminology **T-4**

barnyard
floral
haylike
prune/raisin
resinous
rummy
smoky
sweet
spicy
tobaccolike
vanillin
woody

Working on Costa Rican vanilla beans, Ranadive et al. found that proteinase and peroxidase activities remained fairly steady during growth from the third month until harvest time at the eighth month.[21] Their investigation further showed that the total peroxidase activity was very high in fresh beans throughout the development, while the specific activity was low. However, while the total peroxidase activity decreased, the specific activity showed a marked increase subsequent to the hot water killing and sweating of beans in an oven for 24 h. Ranadive et al. also found at least six substrate-specific glycosidases in maturing vanilla beans. Of these six enzymes, β-glucosidase (optimum pH 6.8) and β-galactosidase (optimum pH 6.8) showed a significant increase in their total and specific activities as the beans matured. Interestingly, the heat resistance of these enzymes also increased greatly as the beans matured. The significance of this can be appreciated from the very important role that β-glucosidase plays during curing after the beans are killed.

Our work on Jamaican and Costa Rican beans showed that p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillic acid (4-hydroxy,3-methoxy benzoic acid), vanillin and a few as-yet-unidentified components are present in green beans in their glucosidic form. We confirmed this by treating the enzyme-deactivated green beans with pure β-glucosidase and measuring the increased levels of these free components in the extracts made from them, and comparing their levels in the untreated enzyme-deactivated green bean extract. Using modern analytical techniques, Leong et al. confirmed the presence of p-hydroxybenzoic acid, p-hydroxybenzaldehyde, vanillic acid (4-hydroxy,3-methoxy benzoic acid) and vanillin only in their glucosidic form in the green ripe Bourbon beans.[27] In contrast to our observations on Jamaican and Costa Rican beans, however, they did not find small amounts of free forms of these monophenols, even in the ripe green beans.

Sagrero-Nieves and Schwartz monitored vanillin, vanillic acid and p-hydroxybenzaldehyde in green vanilla beans harvested every two weeks between August 15 and November 30 (the stage of maturity corresponding to this period was not mentioned).[28] They observed that (free) vanillic acid remained essentially constant in green beans harvested during this period, but vanillin and p-hydroxybenzaldehyde concentration increased from August to November. Ranadive et al. have shown that the green beans contained insignificant amounts of glucovanillin until almost five months after pollination, which rose to about 6.3 percent at full maturity after eight months.[21] Arana found only traces of free vanillin in whole green beans and in split blossom-end yellow beans, while up to 8.8 percent glucovanillin was present in fully mature green beans.[19]

Peroxidase's role in curing of vanilla beans has been studied.[21,23] This heat-resistant enzyme, with its regenerative capacity, has been found to survive various killing and conditioning treatments. Balls and Arana postulated that during curing, and especially during extended conditioning, peroxidase might be responsible for the oxidation of vanillin to produce quinone bodies having a different aroma than vanillin, and thus be partially responsible for the overall vanilla aroma.[20]

Biosynthesis of Glucovanillin in Green Vanilla Beans

It is a fact that most of the vanillin formed in cured beans derives from its immediate precursor, the phenolic glucoside glucovanillin. Glucovanillin starts appearing in green vanilla beans at about four months after pollination. Its level increases dramatically in the last two months of maturation, peaking at harvest maturity, which is reached in eight months.[21]

In studying the biosynthesis of vanillin in vanilla beans, Zenk found that, in the in vitro system, ferulic acid was incorporated in vanillin to a much greater extent than vanillic acid.[29] Zenk concluded that the benzaldehyde derivatives are formed directly from cinnamic acid, rather than benzoic acid. Based on his results, he proposed that ferulic acid is β-oxidized to vanilloyl-CoA, which either can be reduced to vanillin or deacylated to vanillic acid. Whether free ferulic acid is transformed into free vanillin and then bound in the form of a glucoside is not known. Glucovanilin probably is formed from the glucoside of ferulic acid via

the scheme proposed by Zenk. Ferulic acid glucoside, in turn, probably is formed from its precursor, coniferin, which is a glucoside of coniferyl alcohol. The presence of coniferin and coniferyl alcohol in vanilla has been postulated and tentatively identified.[12,29]

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